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(54)

Interfacial viscosification of aqueous systems utilizing sulphonated ionomers.

(57)

The present invention relates to a process for the viscosification of an aqueous liquid which includes the steps of forming a solvent system of an organic liquid or oil and a polar cosolvent, the polar cosolvent being less than about 10 weight percent of the solvent system, the viscosity of the solvent system being less than 1000 cps; dissolving a neutralized sulfonated polymer in the solvent system to form a solution, the concentration of the neutralized sulfonated polymer in the solution being 0.01 to 0.5 weight percent, the viscosity of the solution being less than 200 cps. Thereafter said solution is admixed or contacted with 5 to 500 volume percent aqueous fluid, the aqueous fluid being immiscible with the organic liquid and with the polar cosolvent wherein the neutralized sulphonated polymer transfers from the organic liquid to the aqueous fluid, thereby causing the aqueous phase to thicken.

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3 The present invention relates to a process for
4 the viscosification of an aqueous liquid which includes
5 the steps of forming a solvent system of an organic
6 liquid or oil and a polar cosolvent, the polar cosolvent
7 being less than 15 weight percent of the solvent system,
8 the viscosity of the solvent system being less than
9 1,000 cps; dissolving a neutralized or unneutralized
10 sulphonated polymer (water insoluble) in the solvent
11 system to form a solution, the concentration of the
12 neutralized or unneutralised sulphonated polymer in the solution being
13 0.01 to 0.5 weight percent, the viscosity of the solution
14 being less than 200 cps; and admixing or contacting
15 said solution with 5 to 500 volume percent of the
16 aqueous liquid which is selected from the group consist-
17 ing of water and aqueous acid solution, the aqueous
18 liquid being immiscible with the organic and with the polar
19 cosolvent wherein the neutralised sulphonated polymer
20 transfers : from the organic liquid to the aqueous
21 phase, thereby causing the aqueous phase to gel (i.e.
22 thicken).

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24 The present invention relates to a process for
25 the gelation of an aqueous liquid, wherein the aqueous
26 liquid is selected from water
27 and an aqueous acid solution which includes the steps of
28 forming a solvent system of an organic liquid or oil and
29 a polar cosolvent, the polar cosolvent being less than
30 15 weight percent of the solvent system and with the
31 viscosity of the solvent system being less than 1000 cps, preferably
32 less than 100 cps. Subsequently a neutralised sulphonated polymer is
33 dissolved in the solvent system to form a solution with a
34 concentration of the neutralised sulphonated polymer in the

1 solution being 0.01 to 0.5 weight percent, the viscos-
2 ity of the solution being less than 200 cps. Said
3 solution is admixed or contacted with about 5 to 500 volume
4 percent aqueous liquid, the aqueous liquid being immis-
5 cible with the organic liquid and with the polar cosolvent
6 wherein the neutralized sulphonated polymer transfers from the
7 organic liquid to the aqueous phase, thereby causing the
8 aqueous phase to gel.

9 The gelled aqueous phase having a viscosity
10 greater than 50 cps is formed by the addition of aqueous
11 liquid to the water insoluble solution which comprises
12 a water insoluble, neutralised or unneutralised sulphonated polymer,
13 a nonpolar organic liquid and a polar cosolvent, wherein
14 the solution has a viscosity less than 200 cps. The
15 concentration of neutralised or unneutralised sulphonated polymer in
16 the solution is 0.01 to 0.5 weight percent. Upon the
17 addition of aqueous liquid to the solution, the polar
18 cosolvent and water insoluble, neutralised or unneutralised sulphonated
19 polymer rapidly transfers from the solution to the
20 aqueous phase which undergoes immediate gelation. The
21 nonpolar organic liquid can be removed from the gel by
22 conventional liquid extraction methods. The formation
23 of the aqueous fluid having a viscosity of
24 at least 50 cps from the organic solution having a
25 viscosity less than 200 cps, can be quite rapid of the
26 order of 1 minute to 24 hours, more preferably
27 1 minute to 30 minutes, and most preferably
28 1 minute to 10 minutes, however, this depends
29 on temperature, shear, solvent type, etc.

30 The component materials of the present process
31 generally include a water insoluble, ionomeric polymer
32 such as a water insoluble, neutralized sulfonated poly-
33 mer at a critical concentration level of 0.01 to 0.5
34 weight percent, a nonpolar organic liquid, polar cosol-
35 vent and water or aqueous acid solution.

1 Gelation of an aqueous phase does not occur,
2 if one employs a conventional unsulfonated polymer or a
3 water soluble, neutralized sulfonated polymer in place
4 of the water insoluble, neutralized sulfonated polymer,
5 but rather only classical phase separation occurs.

6 In the present invention, the gelation of the
7 aqueous phase occurs by the formation of geometrically
8 shaped spheres of the water insoluble, neutralized
9 sulfonated polymer within the aqueous phase, wherein the
10 water is encapsulated within these geometrically shaped
11 spheres (so-called water-in-water pseudo-emulsion).
12 During the process, approximately 10 weight percent
13 ~~of the nonpolar organic liquid also transfers to the~~
14 aqueous phase and is encapsulated within these geo-
15 metrically shaped spheres.

16 A second aspect of the present invention
17 relates to the use of these materials in aqueous systems
18 containing large concentrations of acid. The
19 sulfonated polystyrenes which are the preferred embodi-
20 ment of this invention lose their effectiveness (i.e.,
21 as a water-in-water pseudo-emulsion former) in salt
22 water, but are enhanced in acid-containing water.

23 It has been additionally discovered that the
24 addition of a nonionic surfactant can further enhance
25 the gelation of the aqueous acid solution. In acidic
26 solutions, the nonionic surfactant is not needed for
27 stability (25°C), however, the viscosity of these
28 pseudoemulsion systems tends to increase significantly
29 with the addition of small amounts of the nonionic
30 material (typically <0.04g/l).

31 The nonionic surfactants which can be employed
32 in the present invention include
33 polyethylene oxide - polypropylene oxide -
34 block copolymer (polyols), polyoxyethylene sorbitan

1 fatty acid esters, sorbitan fatty acid esters, fatty
2 ~~acids and fatty acid derivatives such as ethoxylated~~
3 fatty acid-Armals (Ethofat^R), amide derivatives such as
4 Armals (Ethomid^R), stearatic acid and stearate deriv-
5 atives, fluorine-containing nonionic surfactants, fatty
6 alcohols, alcohol esters, glycinol esters and poly-
7 ethylene glycol esters. Typical examples of nonionic
8 surfactants are BASF (Pluronic^R), ICI (Atlas^R) ICI
9 (Bris^R) and ICI (Arlacel^R), ICI (Tween^R series), 3M
10 (Fluorad^R) and Shenex (Adol^R), wherein polyethylene
11 oxide - polypropylene oxide - block copolymer (polyols)
12 is preferred. The nonionic surfactant is added to the
13 solvent system at a concentration of about 0.0001 to
14 about 1.0 weight percent of total solvent, more prefer-
15 ably about 0.001 to about 0.5, and most preferably
16 about 0.001 to about 0.005.

17 In general, the water insoluble ionomeric
18 polymer will comprise from 10 to 200 meq. pendant
19 ionomeric groups per 100 grams of polymer, more prefer-
20 ably from 10 to 100 meq. pendant ionomeric groups.
21 The ionic groups may be conveniently selected from
22 carboxylate, phosphonate,
23 and sulfonate, preferably sulfonate groups. In most
24 instances, the ionomers utilized in the present inven-
25 tion are neutralized with the basic materials selected
26 from Groups IA, IIA, IB and IIB of the Periodic Table of
27 Elements and lead, tin and antimony, as well as ammonium
28 and amine counterions. Ionic polymers which are subject
29 to the process of the present invention are illimitable
30 and include both plastic and elastic polymers. Specific
31 polymers include sulfonated polystyrene, sulfonated
32 t-butyl styrene, sulfonated ethylene copolymers,
33 sulfonated propylene copolymers, sulfonated styren /
34 acrylonitrile copolymers, sulfonated styrene/methyl
35 methacrylate copolymers, sulfonated block copolymers of
36 styren /ethylene oxide, acrylic acid c polymers with
37 styrene, sulfonated polyisobutylene, sulfonated ethylene-

1 propylene terpolymers, sulfonated polyisoprene, and
2 sulfonated elastomers and their copolymers. The pre-
3 ferred polymers of the present invention are ethylene-
4 propylene terpolymers and polystyrene, wherein poly-
5 styrene is most preferred.

6 Neutralization of the cited polymers with
7 appropriate metal hydroxides, metal acetates, metal
8 oxides, or ammonium hydroxide etc., can be conducted
9 by means well-known in the art. For example, the
10 sulfonation process as with Butyl rubber containing
11 a small 0.3 to 1.0 mole percent unsaturation can be
12 conducted in a suitable solvent such as toluene,
13 with acetyl sulfate as the sulphonating agent, such as
14 described in U.S. Patent 3,836,511. The resulting
15 sulfonic acid derivative can then be neutralized with
16 a number of different neutralization agents such as a
17 sodium phenolate and similar metal salts. The amounts
18 of such neutralization agents employed will normally be
19 equal stoichiometrically to the amount of free acid in
20 the polymer plus any unreacted reagent which is still
21 present. It is preferred that the amount of neutraliz-
22 ing agent be equal to the molar amount of sulfonating
23 agent originally employed plus 10 percent more to
24 insure full neutralization. The use of more of such
25 neutralization agent is not critical. Usually there
26 is sufficient neutralisation agent to effect at least
27 50 percent neutralization of the sulfonic acid groups
28 present in the polymer, preferably at least 90 percent,
29 and most preferably substantially complete neutralization
30 of such acid groups should be effected.

31 The degree of neutralization of said ionomeric
32 groups may vary from 0 (free acid form) to greater than
33 100 mole percent, preferably 50 to 100 percent. With
34 the utilization of neutralized ionomers in this present
35 invention, it is preferred that the degree of neutral-

1 ization be substantially complete, that is with no
2 substantial free acid present and without substantial
3 excess of the base other than that needed to ensure
4 neutralization. The neutralized ionomers possess
5 greater thermal stability compared to its acid form.
6 Thus, it is clear that the polymers which are normally
7 utilized in the present invention comprise substantially
8 neutralized pendant groups, and in fact, an excess of
9 the neutralizing material may be utilized without
10 defeating the objects of the present invention.

11 The ionomeric polymers of the present inven-
12 tion may vary in number average molecular weight from
13 1,000 to 10,000,000 preferably from 5,000 to 500,000,
14 most preferably from 10,000 to 200,000. These polymers
15 may be prepared by methods known in the art, for example,
16 see U.S. Patent 3,642,728.

17 The preferred ionic copolymers for use in the
18 present invention, e.g., sulfonated polystyrene and
19 substituted derivatives thereof, may be prepared by
20 the procedures described in U.S. Patent 3,870,841,
21 filed October 2, 1972, in the names of H. S. Makowski,
22 R. D. Lundberg and G. H. Singhal.

23 The water insoluble, ionomeric polymers may be
24 incorporated into the organic liquid at a level of from
25 0.01 to 0.5 weight percent and more preferably from 0.01
26 to 0.4 weight percent, based on the organic liquid and
27 the polar cosolvent.

28 Specific examples of preferred ionomeric
29 polymers which are useful in the present invention
30 include sulfonated polystyrene, sulfonated poly-t-butyl
31 styrene, sulfonated polyethylene (substantially non-
32 crystalline), and sulfonated ethylene copolymers,
33 sulfonated polypropylene (substantially noncrystalline),

1 and sulfonated polypropylene copolymers, sulfonated
2 styrenemethyl methacrylate copolymers, (styrene)-acrylic
3 acid copolymers, sulfonated polyisobutylene, sulfonated
4 ethylene-propylene terpolymers, sulfonated polyisoprene,
5 sulfonated polyvinyl toluene and sulfonated polyvinyl
6 toluene copolymers.

7 The ionomeric polymers of the present inven-
8 tion may be prepared prior to incorporation into the
9 organic solvent, or by neutralization of the acid form
10 insitu. For example, preferably the acid derivative is
11 neutralized immediately after preparation. For example,
12 if the sulfonation of polystyrene is conducted in solu-
13 tion, then the neutralization of that acid derivative
14 can be conducted immediately following the sulfonation
15 procedure. The neutralized polymer may then be isolated
16 by means well-known to those skilled in the art, i.e.,
17 coagulation, steam stripping, or solvent evaporation,
18 because the neutralized polymer has sufficient thermal
19 stability to be dried for employment at a later time in
20 the process of the present invention. It is well-known
21 that the unneutralized sulfonic acid derivatives do not
22 possess good thermal stability and the above operations
23 avoid that problem.

24 It is also possible to neutralize the acid
25 form of these polymers in situ; however, this is not a
26 preferred operation, since in situ neutralization
27 requires preparation of the sulfonic acid in the organic
28 liquid which is to be subjected to the present process,
29 or the acid form of the ionic polymer must be dissolved
30 in said organic liquid. The latter approach may involve
31 handling of an acid form of an ionic polymer which has
32 limited thermal stability. Therefore, it is quite
33 apparent that the preparation and isolation of a neu-
34 tralized ionic polymer affords the maximum latitude in
35 formulation, less problems in handling polymers of

1 limited thermal stability and maximum control over the
2 final mixture of ionic polymer, polar cosolvent and
3 organic liquid.

4 The organic liquids, which may be utilized
5 in the present invention, are selected with relation
6 to the ionic polymer and vice-versa. The organic liquid
7 may be selected from
8 aromatic hydrocarbons, cyclic aliphatic ethers, ali-
9 phatic ethers, organic aliphatic esters and mixtures
10 thereof.

11 Specific examples of organic liquids to be
12 employed with the various types of polymers are:

13 <u>Polymer</u>	<u>Organic Liquid</u>
14 sulfonated polystyrene	benzene, toluene, ethyl
15	benzene, methylethyl
16	ketone, xylene, styrene,
17	ethylenedichloride,
18	methylene chloride.
19 sulfonated poly-t-butyl-	benzene, toluene, xylene,
20 styrene	ethyl benzene, styrene,
21	t-butyl styrene, aliphatic
22	oils, aromatic oils, hexane,
23	heptane, decane, nonane.
24 sulfonated ethylene-	pentane, aliphatic and
25 propylene terpolymer	aromatic solvents, oils
26	such as Solvent "100
27	Neutral", "150 Neutral"
28	and similar oils, benzene,
29	diesel oil, toluene,
30	xylene, ethyl benzene,
31	pentane, hexane, heptane,

1		octane, isooctane, nonane,
2		decane aromatic solvents,
3		ketone solvents.
4	sulfonated styrene-methyl-	dioxane, halogenated ali-
5	methacrylate copolymer	phatics, e.g., methylene
6		chloride, tetrahydrofuran.
7	sulfonated polyisobutylene	saturated aliphatic hydro-
8		carbons, diisobutylene,
9		triisobutylene, aromatic
10		and alkyl substituted
11		aromatic hydrocarbons,
12		chlorinated hydrocarbons,
13		n-butyl ether, n-amyl,
14		ether, methyl oleate,
15		aliphatic oils, oils pre-
16		dominantly paraffinic
17		in nature and mixtures
18		containing naphthenic
19		hydrocarbons. "Solvent 100
20		Neutral", "Solvent 150
21		Neutral" and all related
22		oils, low molecular weight
23		polymeric oils such as
24		squalene, white oils and
25		process oils having 60
26		percent or less aromatic
27		content.
28	sulfonated polyvinyl	toluene, benzene, xylene,
29	toluene	cyclohexane, ethyl benzene,
30		styrene, methylene chlo-
31		ride, ethylene dichloride.

32 The process of the present invention includes
33 incorporating a polar cosolvent, for example, a polar

1 cosolvent in the mixture of organic liquid and water
2 insoluble ionomer to solubilize the pendant ionomeric
3 groups. The polar cosolvent will usually have a solubility
4 parameter of at least 10.0, preferably at least
5 11.0 and is water miscible and may comprise from 0.1
6 to 15.0 weight percent, preferably 0.1 to 5.0 weight
7 percent of the total mixture of organic liquid, water
8 insoluble ionomeric polymer, and polar cosolvent. The
9 solvent system of polar cosolvent and organic liquid
10 in which the water insoluble neutralized sulfonated
11 (ionomeric) polymer is dissolved contains less than 10
12 weight percent of the polar cosolvent, more preferably
13 0.1 to 5.0 weight percent, and most preferably 0.1
14 to 5.0 weight percent. The viscosity of the solvent
15 system is less than 1,000 cps, more preferably less than
16 800 cps and most preferably less than 500 cps.

17 Normally, the polar cosolvent will be a liquid
18 at room temperature; however, this is not a requirement.
19 It is preferred, but not essential, that the polar
20 cosolvent be soluble or miscible with the organic liquid
21 at the levels employed in this invention. The polar
22 cosolvent may be selected from water soluble alcohols,
23 including di- or tri- functional alcohols, amines, amides,
24 acetamides, phosphates, or
25 lactones and mixtures thereof. Especially preferred
26 polar cosolvents are aliphatic alcohols such as methanol,
27 ethanol, n-propanol, isopropanol, 1,2-propane diol,
28 monoethyl ether of ethylene glycol, and n-ethylformamide.

29 The amount of aqueous fluid added to the
30 solution of water insoluble, neutralised or unneutralised
31 sulphonated polymer, organic liquid and polar cosolvent
32 having a viscosity of less than 2,000 cps (preferably less
33 than 200 cps), is 5 to 500 volume percent of water, more
34 preferably 10 to 300 volume percent water, most preferably
35 10 to 200 volume percent water.

1 The aqueous acid solution of hydrochloric
2 acid, in which the water insoluble neutralised or unneutralised
3 sulphonated polymer thickens, preferably contains less than about 40
4 weight percent acid, more preferably about 0.1 to about
5 30 weight percent, and most preferably about 1.0 to
6 about 20 weight percent.

7

8 The following examples will demonstrate the
9 performance of sulfonated polystyrene of varying sul-
10 fonate levels in several specific aqueous environments.

11 EXAMPLE 1

12 It has been observed that under certain
13 conditions, if a hydrocarbon solution containing a low
14 concentration of a sulfonated polystyrene or sulfonated
15 EPDM is mildly agitated with water for a short period
16 of time, a pseudo-emulsion is formed. In the initial
17 formation stage, the type of pseudo-emulsion produced
18 in these systems has a continuous aqueous phase while
19 the hydrocarbon medium is the dispersed phase. It is
20 believed that the sulfonated polymer stabilizes the
21 hydrocarbon/water interface. Upon standing for a short
22 period of time after mixing has occurred, it is observed
23 that approximately 90 percent of the initial hydrocarbon
24 solvent can be separated from the system leaving behind
25 a pseudoemulsion system characterized as a water-in-
26 water pseudoemulsion. Addition of a small amount of
27 nonionic surfactant can be added to facilitate this
28 process. Experimental evidence indicates that free
29 passage of nonpolar organic solvent occurs through the
30 sulfonated polymer membrane and the hydrocarbon solvent
31 is replaced within each sphere by water as the nonpolar,
32 organic solvent passes through the membrane.

1 As shown in Table I, the essential material
2 needed for the formation of a pseudo-emulsion system in
3 a hydrocarbon/water environment is the water insoluble,
4 neutralized sulfonated polymer. Table I shows that the
5 addition of water to a No. 2 diesel oil (or xylene)
6 solution containing tridecyl alcohol as a cosolvent
7 and/or unsulfonated EPDM (Socabu 55) or polystyrene
8 (Styron 666) results in a classic phase separation of
9 the hydrocarbon and water phases. On the other hand,
10 spontaneous formation of a pseudo-emulsion system occurs
11 in the presence of the sulfonated polymer. In addition,
12 it has been observed that more stable pseudo-emulsion
13 systems are produced with increasing sulfonation level.
14 The nature of the counterion does not impair the inter-
15 facial activity of the polymer.

16 Further confirmation of the interfacial
17 activity of these sulfonated polymers can be obtained
18 utilizing viscosity measurements. The viscosity of
19 several water-in-water pseudo-emulsions as a function of
20 the polymer concentration is shown in Table II. It is
21 readily apparent that due to the particular "macroscopic"
22 structures formed in the aqueous phase, significant
23 viscosification occurs as compared to the dissolution of
24 a water soluble polymer of equivalent molecular weight
25 and concentration. The viscosity of the pseudo-emulsion
26 system at high polymer levels rises, while within the
27 concentration range between approximately 1 and 5 g/l,
28 the viscosity is essentially constant. Only when rather
29 low polymer levels are reached does the viscosity begin
30 to decline again. A comparison of the EPDM and poly-
31 styrene data indicates that the nature of the backbone
32 chain may have little influence on the viscosity of
33 the system, while the sulfonate level is of paramount
34 importance. These results can be rationalized by
35 assuming that the sulfonated polymer resides at the
36 water-water interface. This latter observation is

1 supported through the use of light microscopy. Under
2 low magnification (approximately 100X) the structural
3 details of the pseudo-emulsion system can be observed.
4 In the first place, a large number of spheres consti-
5 tutes a typical pseudo-emulsion system. Secondly, each
6 pseudo-emulsion particle is a spherical structure in
7 which a large volume of water is contained with the
8 polymer film. The continuous phase outside of each
9 particle is identical in composition to the internal
10 aqueous phase.

11 EXAMPLE 2

12 Table II shows the relationship between the
13 viscosity of the pseudo-emulsion phase, formed with
14 polystyrene containing various sulfonation levels,
15 as a function of polymer concentration. The viscosity
16 tends to rise at very low polymer concentrations.

17 Outside of this concentration
18 regime, the viscosity remains constant to rather high
19 polymer levels (~0.5 g/dl.) The viscosity of the
20 pseudo-emulsion at a particular polymer concentration
21 does increase with higher sulfonation levels. Undoubt-
22 edly, this observation is related to both the sphere
23 size and packing within the aqueous phase.

TABLE I

FORMATION OF WATER-IN-WATER PSEUDO-EMULSION
(50 HYDROCARBON/50 WATER)

	<u>Material</u>	<u>Water/Water Pseudo-Emulsion Formed</u>	
6	Tridecyl Alcohol	No	
7	Socabu 55 or Styron 666	No	
8	Socabu 55/Tridecyl Alcohol	No	
9	Zinc Neutralized (10-30 meq.) EPDM	Yes	
10	Magnesium and Calcium Neutralized (10 meq.) EPDM	Yes	
11	Magnesium and Calcium Neutralized (10 meq.) EPDM	Yes	
12	Tridecyl Alcohol		
13	Unneutralized Sulfonated (25 meq.) EPDM	Yes	
14	Tridecyl Alcohol	Yes	
15	Sodium Sulfonated (1-6 mole %) Polystyrene	Yes	
16	Zinc Sulfonated (1-3 mole %) Polystyrene	Yes	

TABLE II
 VISCOSITY* - POLYMER CONCENTRATION DATA
 OF A TYPICAL PSEUDO-EMULSION SYSTEM

	Material	Polymer Concentration (g/l)	Viscosity (cps)
4	Sulfonated Polystyrene		
5	(Sodium Salt - 1.7 mole %)		
6		0.25	210
7		0.5	295
8		1.25	315
9		2.5	320
10		5.0	340
11			
13	Sulfonated EPDM		
14	(Magnesium Salt - 10 meq.)		
15		0.50	160
16		1.25	204
		2.5	210
		5.0	210

17 *Viscosity measured with a Brookfield^R viscometer at 30 RPM.

TABLE III

VISCOSITY* - POLYMER CONCENTRATION DATA OF SEVERAL PSEUDO-EMULSION SYSTEMS FORMED WITH SEVERAL SODIUM SALTS OF SULFONATED POLYSTYRENES

	Material (mole %)	Polymer Level (g/l)	viscosity (cps)
4			
5	3.0	0.12	280
6		0.5	430
7		1.0	480
8		2.0	490
9	4.19	0.12	380
10		0.25	440
11		0.5	570
12		2.0	820
13	6.05	0.12	420
14		0.25	540
15		0.5	820
16		2.0	950

17 *viscosity measured with a Brookfield^R viscometer at 30 RPM.

1 EXAMPLE 3

2 Due to the aqueous nature of the fluid within
3 the thin membrane of the pseudo-emulsion particle, we
4 observe dramatic changes in viscosity as the shear rate
5 is modified. Table IV shows the viscosity behavior of
6 a typical pseudo-emulsion system in fresh water as a
7 function of the rate of shear. At low shear rates, the
8 viscosity is high, while a decrease is found at higher
9 shear. Furthermore, we observe a marked viscosity
10 decrease as the overall shear rate is increased, which
11 is typical behavior of all pseudo-emulsion systems (i.e.
12 ~~fresh, salt, acid or basic environments).~~ In this
13 particular example, an order of magnitude viscosity
14 change is found over a relatively modest shear rate
15 range. Furthermore, we observe that this behavior is
16 reversible (which again is typical behavior of a pseudo-
17 emulsion system) within the shear rate range presented
18 in this example.

TABLE IV

VISCOSITY - SHEAR RATE BEHAVIOR OF A TYPICAL
PSEUDO-EMULSION SYSTEM IN FRESH WATER

	<u>Material</u>	<u>Shear Rate (sec⁻¹)</u>	<u>Viscosity (cps)</u>
1			
2			
3			
4	<u>Material</u>		
5	Sulfonated Polystyrene		
6	(6.05 mole % - Sodium Salt)	0.4	470
7		0.8	390
8		2.0	190
9		4.0	120
10		8.0	70
11		16.0	68
12		40.0	52
13		79.0	45

1 It is evident from these discussions that this
2 invention claims a markedly different process and
3 product than that described in some previous patents
4 covering the same class of polymers in similar mixed
5 solvents. The prior applications were specifically
6 directed at gelation of a hydrocarbon phase by contact
7 of mixed solvents with an aqueous phase and extraction
8 of a water miscible cosolvent from the organic phase,
9 thereby permitting association of the ionic groups and
10 gelation. In this and copending applications, we claim
11 viscosification of the aqueous phase. Such a claim
12 would certainly appear inconsistent and unexpected in
~~13 view of those prior patent applications. This discus-~~
14 sion will attempt to explain these observations on a
15 molecular scale.

16 We assume that the ionic polymers of this
17 study are dissolved in an organic diluent containing
18 a polar cosolvent (alcohol) via selected solvation.
19 The resulting ionic polymer is thereby homogeneously
20 dissolved without substantial aggregation. Now, if
21 sufficient polymer is present (i.e. >1%) for a conven-
22 tional high molecular weight polymer, there is an
23 overlap of the polymer coils (i.e., they intermingle
24 and entangle). Under these conditions, if the cosolvent
25 is removed (i.e., by contact with water), then the
26 resultant aggregation of the ionic groups results in a
27 total network or polymer gelation of the hydrocarbon
28 phase occurs.

29 However, the unexpected observation which is
30 the basis for the present invention is that, if the
31 polymer concentration in the hydrocarbon phase is less
32 than 0.5% or so, the polymer coils no longer are in the
33 overlap regime. Thus, entanglements between polymer
34 chains do not obtain. Under these conditions, contact
35 of the solution with water does not result in gelation,

1 but rather the polymer forms the pseudoemulsion phase
2 described herein. Thus, polymer concentration is the
3 major variable and dominates which phase (aqueous or
4 hydrocarbon) is viscosified.

5 EXAMPLE 4

6 Table V shows the effectiveness of 6.05 mole
7 percent sulfonated polystyrene as a viscosifier for a 10
8 percent hydrochloric acid solution. The data indicate
9 that acid solutions containing pseudo-emulsion particles
10 can be used to significantly enhance the viscosity
11 of the aqueous acid phase even though the sulfonated
12 polymer is hydrocarbon soluble. The viscosity of the
13 hydrocarbon solvent containing the sulfonated polymer is
14 less than 100 centipoise. The data also show that the
15 pseudo-emulsion phase can be produced over a wide range
16 of "dilution" with little change in viscosity. Each
17 individual sphere is capable of expanding to accommodate
18 the increased aqueous acid phase volume by absorption
19 through the polymer membrane. The size of each sphere
20 increases, but the volume fraction of spheres remains
21 constant.

TABLE V

VISCOSITY (30 RPM) OF PSEUDO-EMULSION*
VERSUS VOLUME OF HCl SOLUTION (10 %)

	<u>Solution Volume (ml)**</u>	<u>Viscosity (cps)</u>
5	25	696
6	30	500
7	35	384
8	40	544
9	45	592

10 *Initial solution concentrations: 15 ml. at 0.5 g/l of
11 6.05 mole % sulfo-polystyrene.

12 **Amount of acid solution used to prepare pseudo-emulsion phase.

1 EXAMPLE 5

2 Table VI shows the effectiveness of utilizing
3 a nonionic surfactant (BASF Pluronic^R F-108) at very low
4 concentrations in the preparation of pseudo-emulsions in
5 10 weight percent acid solution. The sulfonated poly-
6 styrene was initially dissolved in a xylene/methanol
7 solvent system. The data indicates that these acid
8 solutions containing pseudo-emulsion particles in
9 conjugation with minute amounts of nonionic surfactant
10 can be used to significantly enhance the viscosity of
11 the aqueous acid solution even though the polymer is
12 wholly hydrocarbon soluble. Moreover, the data show
13 that the surfactant produces marked enhanced viscosity
14 over that observed without surfactant present (Table V).
15 The data also show that these pseudo-emulsion systems
16 can be produced over a wide range of "dilution" with
17 relatively minor modification in viscosity.

18

TABLE VI

19 VISCOSITY (12 RPM) OF PSEUDO-EMULSION (NaSPS) VERSUS
20 VOLUME OF HCl SOLUTION (0.04 g/l NONIONIC SURFACTANT)

21	<u>Solution Volume (ml.)*</u>	<u>Viscosity (cps)</u>
22	25	5,831
23	35	4,582
24	45	5,831

25 ~~*Amount of acid solution used to prepare pseudo-emulsion~~
26 phase. Concentration of acid is 10.0 weight percent.

CLAIMS:

1 1. A process for forming a thickened aqueous
2 fluid, wherein such aqueous fluid is selected from
3 water and aqueous acid solution^{and}
4 having a viscosity of at least about 50 cps which
5 comprises .:

6 (a) forming a solvent system comprising an organic
7 liquid and a polar cosolvent, said polar cosolvent being
8 less than about 10 weight percent of said solvent
9 system, the viscosity of said solvent system being less
10 than about 1000 cps;

11 (b) dissolving a water insoluble, unneutral-
12 ized or neutralised sulphonated polymer in said solvent
13 system to form a solution, the concentration of said
14 unneutralized or neutralised sulphonated polymer in said
15 solution being about 0.01 to about 0.5 weight percent, the
16 viscosity of said solution being less than about 2000
17 cps; and

18 (c) adding about 5 to about 500 volume
19 percent of said aqueous fluid to said solution, said aqueous
20 fluid being immiscible with said solution and with said
21 polar cosolvent wherein said water insoluble, neutralised
22 sulphonated polymer transfers from said organic liquid
23 to said aqueous fluid causing the viscosity of said
24 aqueous fluid to increase to at least 50 cps.

25 2. A process according to claim 1 which
26 includes a means for removing said organic liquid from
27 said aqueous fluid.

28 3. A process according to either of claims 1 and 2 wherein
29 said unneutralized or neutralized sulfonated polymer has

1 about 10 (free acid) to about 200 meq. of pendant SO_3H groups per
2 100 grams of polymer.

3 4. A process according to any one of the preceding claims
4 wherein the sulphonate groups are neutralised with a metal counterion
5 selected from antimony, tin, lead and Groups IA, IIA, IB or IIB of
6 the Periodic Table of Elements.

7 5. A process according to any one of the preceding claims
8 wherein said neutralised sulphonated polymer is formed from an
9 elastomeric or thermoplastic polymer.

10 6. A process according to any one of the preceding claims
11 wherein said polar cosolvent is selected from aliphatic amines,
12 mono-, di or tri- functional aliphatic alcohols, water miscible
13 amides, acetamides, phosphates, lactones and mixtures thereof.

14 7. A process according to any one of the preceding claims
15 wherein said organic liquid is selected from aromatic hydrocarbons,
16 ketones, chlorinated aliphatic hydrocarbons, aliphatic hydrocarbons,
17 cyclic aliphatic ethers, aliphatic ethers, organic aliphatic esters
18 and mixtures thereof.

19 8. A process according to any one of the preceding claims
20 wherein said aqueous fluid has a nonionic surfactant incorporated therein.

21 9. A process according to claim 8 wherein said nonionic
22 surfactant is selected from BASF (Pluronic^R), ICI (Atlas^R) ICI
23 (Bris^R) and ICI (Arlacel^R), ICI (Tween^R series), 3M (Fluorad^R) and
24 Shenex (Adol^R), preferably polyethylene oxide - polypropylene oxide -
25 block copolymer (polyols).

26 10. A process according to any one of the preceding claims
27 wherein the viscosity of the solvent system is less than 100 cps and
28 the viscosity of the solution formed by dissolving the polymer in
29 said solvent system is less than 200 cps.



European Patent
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EUROPEAN SEARCH REPORT

0093596

Application number

EP 83 30 2437

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. 3)
X	US-A-4 282 130 (R.D. LUNDBERG et al.) * Column 1, lines 10-27; column 4, lines 31-53; column 7, lines 52-62 *	1,3-7	C 08 J 3/08 C 08 L 57/06 B 01 J 13/00
X	US-A-4 322 329 (R.D. LUNDBERG et al.) * Column 1, lines 14-31; column 4, lines 36-58; column 6, lines 9-20 *	1,3-7	
A	US-A-4 313 862 (R.D. LUNDBERG et al.) * Column 1, lines 15-28; column 4, lines 10-39; column 5, line 59 - column 6, line 68 *	1,4,5,7	
A	US-A-3 770 682 (HUBBARD et al.) * Column 6, lines 58-69 *	1	TECHNICAL FIELDS SEARCHED (Int. Cl. 3) C 08 J C 08 L C 09 D C 09 K E 21 B B 01 J
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 14-07-1983	Examiner KERRES P.M.G.
<p>CATEGORY OF CITED DOCUMENTS</p> <p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</p> <p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document</p>			